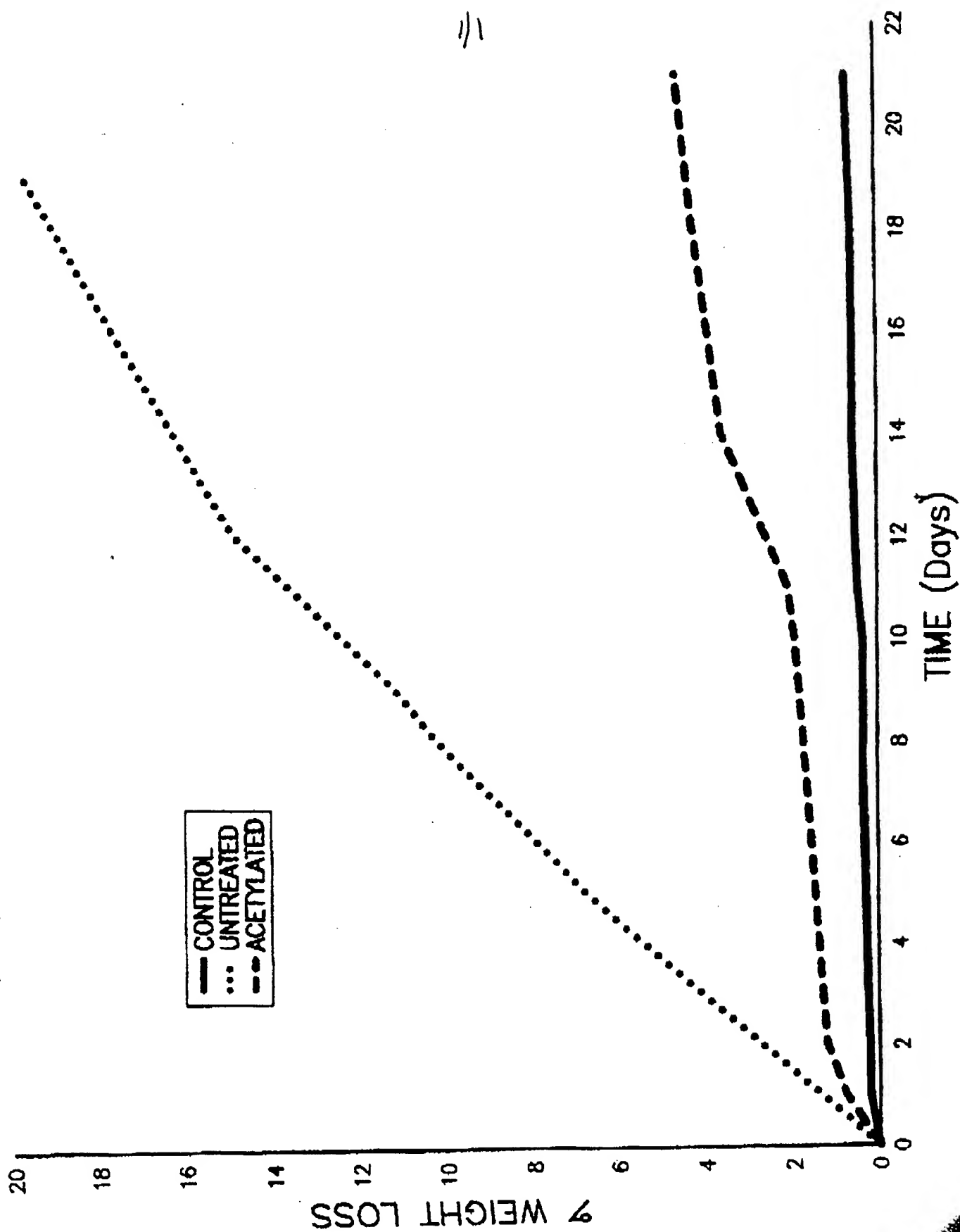


% WEIGHT LOSS OF OIL AND WATER MIXED WITH FIBRE



The  
Patent  
Office

PCT/GB 91/01711

08/050000

The Patent Office  
Cardiff Road  
Newport  
Gwent  
NP9 1RH

REC'D 07 JAN 1992  
WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 62(3) of the Patents and Designs Act 1907, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the Patent application identified therein.

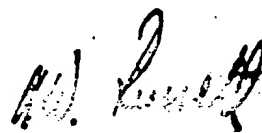
In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or the inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered. #2

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

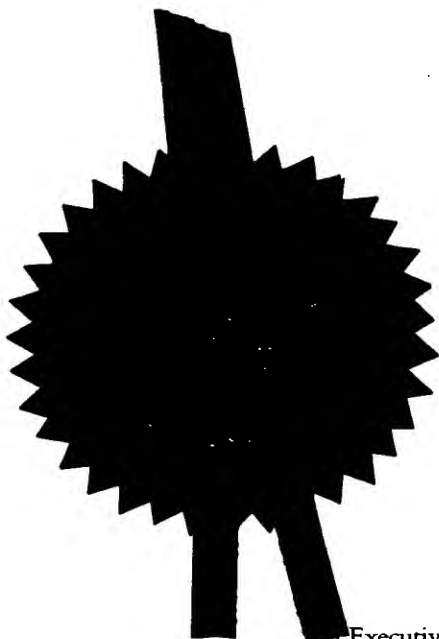
PRIORITY DOCUMENT

Signed



Dated

16 DEC 1991



**PATENT'S ACT 1977****- 3 OCT 1990**

PATENTS FORM NO. 1/77 (Revised 1982)

(Rules 16, 19)

The Comptroller  
The Patent Office

-40CT 190800388123

PAT 1 77 UC

15.00

NID

9021509.6

**REQUEST FOR GRANT OF A PATENT****THE GRANT OF A PATENT IS REQUESTED BY THE UNDERSIGNED ON THE BASIS OF THE PRESENT APPLICATION**

I Applicant's or Agent's reference (Please insert if available) **PBA/86410**

II Title of invention **IMPROVEMENTS IN OR RELATING TO THE ABSORPTION OF HYDROPHOBIC WATER-IMMISCIBLE LIQUID**

III Applicant or Applicants (See note 2)

**DAVID J. ROBSON**  
Name (First or only applicant)

**United Kingdom**  
Country

State ..... ADP Code No. **5721899001**  
Address **Lleiniaw, Dwyran, Anglesey, Gwynedd LL61 6YG.** **7p**

Name (of second applicant, if more than one) **J. MARK LAWTHER**  
**United Kingdom**

Country ..... State .....  
Address **47 Bro Emrys, Tal-y-Bont, Bangor, Gwynedd LL57 3YS.**

**THIRD INVENTOR - CONTINUED OVER**

IV Inventor (see note 3)

(a) The applicant(s) ~~is~~/are the  
~~joint~~/joint inventor(s)

or

~~(b) An statement on Patents Form~~  
~~No 7/77 is/will be furnished~~  
~~xxxxxxxxxxxxxxxxxxxx~~

V Name of Agent (if any) (See note 4)

**MARKS & CLERK**

ADP CODE NO

**18004**

VI Address for Service (See note 5)

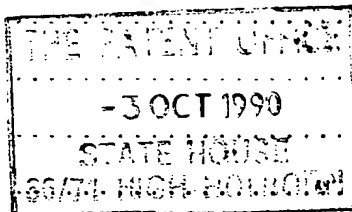
**Suite 301, Sunlight House,**  
**Quay Street, Manchester. M3 3JY.**

VII Declaration of Priority (See note 6)

Country

Filing date

File number



VIII The Application claims an earlier date under Section 8(3), 12(6), 15(4), or 37(4) (See note 7)

Earlier application or patent number ..... and filing date .....

**PATENTS ACT 1977**

PATENTS FORM NO. 1/77 (Rvised 1982)

(Rul s 16, 19)

The Comptroller

Th P tent Office

-3 OCT 1990

9021309.0

**REQUEST FOR GRANT OF A PATENT****THE GRANT OF A PATENT IS REQUESTED BY THE UNDERSIGNED ON THE BASIS OF THE PRESENT APPLICATION**I Applicant's or Agent's reference *(Please insert if available)*

II Title of invention

III Applicant or Applicants *(See note 2)***THIRD APPLICANT**Name *(First or only applicant)* **SARA HUGHES**Country **United Kingdom**

State

ADP Code No.

**5.7319/5001**Address **4 Tan Y Bryn Terrace, Bangor, Gwynedd LL57 1HS.**Name *(of second applicant, if more than one)*

Country

State

Address

IV Inventor *(see note 3)*

(a) The applicant(s) is/are the sole/joint inventor(s)

or

(b) A statement on Patents Form No 7/77 is/will be furnished

V Name of Agent *(if any)* *(See note 4)*

ADP CODE NO

VI Address for Service *(See note 5)*VII Declaration of Priority *(See note 6)*

Country

Filing date

File number

VIII The Application claims an earlier date under Section 8(3), 12(6), 15(4), or 37(4) *(See note 7)*

Earlier application or patent number ..... and filing date .....

IX Check List (To be filled in by applicant or agent)

- |   |  |
|---|--|
| <p>A The application contains the following number of sheet(s)</p> <p>1 Request ..... 1 ..... Sheet(s)</p> <p>2 Description ..... 6 ..... Sheet(s)</p> <p>3 Claim(s) ..... Sheet(s)</p> <p>4 Drawing(s) ..... 1 ..... Sheet(s)</p> <p>5 Abstract ..... Sheet(s)</p> | <p>B The application as filed is accompanied by:-</p> <p>1 Priority document .</p> <p>Translation of priority document</p> <p>3 Request for Search.....</p> <p>4 Statement of Inventorship and Right to Grant.....</p> |
|---|--|

X It is suggested that Figure No.....of the drawings (if any) should accompany the abstract when published

XI Signature (See note 8)

NOTES:

1. This form, when completed, should be brought or sent to the Patent Office together with the prescribed fee and two copies of the description of the invention, and of any drawings.
2. Enter the name and address of each applicant. Names of individuals should be indicated in full and the surname or family name should be underlined. The names of all partners in a firm must be given in full. Bodies corporate should be designated by their corporate name and the country of incorporation and, where appropriate, the state of incorporation within that country should be entered where provided. Full corporate details, eg a "corporation organised and existing under the laws of the State of Delaware, United States of America", trading styles, eg "trading as xyz company", nationality, and former names, eg "formerly (known as) ABC Ltd" are *not* required and should *not* be given. Also enter applicant(s) ADP Code No.(if known).
3. Where the applicant or applicants is/are the sole inventor or the joint inventors, the declaration (a) to that effect at IV should be completed, and the alternative statement (b) deleted. If, however, this is not the case the declaration (a) should be struck out and a statement will then be required to be filed upon Patent Form No 7/77.
4. If the applicant has appointed an agent to act on his behalf, the agent's name and the address of his place of business should be indicated in the spaces available at V and VI. Also insert agent's ADP Code No. (if known) in the box provided.
5. An address for service in the United Kingdom to which all documents may be sent must be stated at VI. It is recommended that a telephone number be provided if an agent is not appointed.
6. The declaration of priority at VII should state the date of the previous filing and the country in which it was made and indicate the file number, if available.
7. When an application is made by virtue of section 8(3), 12(6), 15(4) the appropriate section should be identified at VIII and the number of the earlier application or any patent granted thereon identified.
8. Attention is directed to rules 90 and 106 of the Patent Rules 1982.
9. Attention of applicants is drawn to the desirability of avoiding publication of inventions relating to any article, material or device intended or adapted for use in war (Official Secrets Acts, 1911 and 1920). In addition after an application for a patent has been filed at the Patent Office the comptroller will consider whether publication or communication of the invention should be prohibited or restricted under section 22 of the Act and will inform the applicant if such prohibition is necessary.
10. Applicants resident in the United Kingdom are also reminded that, under the provisions of section 23 applications may not be filed abroad without written permission or unless an application has been filed not less than six weeks previously in the United Kingdom for a patent for the same invention and no direction prohibiting publication or communication has been given or any such direction has been received.

IMPROVEMENTS IN OR RELATING TO  
THE ABSORPTION OF HYDROPHOBIC WATER-IMMISCIBLE LIQUIDS

The present invention relates to the absorption of hydrophobic water-immiscible liquids, particularly but not exclusively for cleaning-up liquid spillages as well as to materials and products for effecting the absorption of hydrophobic water-immiscible liquids.

A wide variety of hydrophobic water-immiscible liquids absorbents have been used in the past to clean up liquid spillage in water and from around machinery (particularly to clean up oil spillage). These absorbents fall into two main categories: firstly synthetic polymers (e.g. polypropylene) and secondly natural plant based materials such as straw, peat and sawdust. However, both of these categories of materials have their disadvantages. In particular, the synthetic polymers (e.g. polypropylene) are relatively expensive in comparison with plant material whereas plant material itself has a combination of hydrophilic and hydrophobic properties and attracts both water and hydrophobic water-immiscible liquids. An additional disadvantage of these natural products is that they are biodegradable and deteriorate during storage.

A further prior proposal made by Midland Silicones (part of DOW Corning) is the use of silanated sawdust to render the sawdust more hydrophobic and more attractive to hydrophobic water-immiscible liquids. The silanated saw dust was particularly developed to absorb oil. This proposal has the disadvantage that silanation is a relatively expensive chemical modification.

A further proposal based on the use of natural products is disclosed in EP-A-0 094 363 which describes a plant material based product specifically as an oil absorbing composition which comprised at least 50% by weight of hydrophobic cellulose pulp blended with 30%-50% of an organic cellulose paper pulp filler. The cellulose pulp is rendered hydrophobic by a conventional non-bonding hydrophobing treatment including inter alia a conventional sizing treatment. However, a disadvantage of the oil absorbing products disclosed in EP-A-0 094 363 is that they only float on water for a limited time.

It is an object of the present invention to obviate or mitigate the abovementioned disadvantages.

According to a first aspect of the present invention there is

provided for use as an absorbent of hydrophobic water-immiscible liquids, lignocellulose material which has been rendered attractive to hydrophobic water-immiscible liquids by chemical reaction of hydroxyl groups in the lignocellulose. Examples of hydrophobic water-immiscible liquids are crude and refined oil, solvents such as white spirit, toluene, benzene and pesticide residues.

For convenience the lignocellulose material which has been rendered attractive to hydrophobic water-immiscible liquids by chemical reaction of hydroxyl groups in the lignocellulose is referred to hereinafter as the "modified lignocellulose".

According to a second aspect of the invention there is provided a method of absorbing hydrophobic water-immiscible liquids comprising treating the liquid with the modified lignocellulose.

A third aspect of the invention provides an article for absorbing hydrophobic water-immiscible liquids comprising the modified lignocellulose within a covering material through which liquid may pass.

A fourth aspect of the invention comprises the modified lignocellulose in sheet form.

The preferred form of the modified lignocellulose for use in the invention is esterified lignocellulose, ie lignocellulose in which the phenolic hydroxyl groups and possibly also the hydroxyl groups of the cellulose and the hemicellulose are esterified. Preferably the acid residues in the esterified lignocellulose are of the formula  $\text{Alk-C(O)-O}$  in which Alk is an alkyl group of 1-4 carbon atoms. Processes for producing esterified lignocellulose are already known (see for example EP-A-0 213 252) and such prior processes are suitable for producing modified lignocellulose for use in this invention. Typically however the esterification will be effected by treating the lignocellulose with the corresponding anhydride, removing excess anhydride, and then heating the lignocellulose in an oven, eg in the temperature range 90-150°C. The degree of esterification should be sufficient to render the lignocellulose attractive to hydrophobic water-immiscible liquids whilst still retaining internal hydrogen bonding to maintain the integrity of the fibre. Usually, the degree of esterification will be such as to provide a 12-20% weight gain for the lignocellulose.

The preferred method of esterification is by acetylation since acetic anhydride which is of relatively low cost may be used as the

acetylating agent.

Treatments other than esterification which may be used for rendering lignocellulose attractive to hydrophobic water-immiscible liquids include reaction with an isocyanate so as to convert the hydroxyl groups of the lignocellulose to urethane linkages. Examples of suitable isocyanates are monoisocyanates such as propyl isocyanate, butyl isocyanate and octadecyl isocyanate.

The agent used for rendering the lignocellulose attractive to water-immiscible liquids may be of di-or higher functionality so as to provide a degree of cross-linking in the lignocellulose.

The preferred lignocellulose used as starting material for modification treatment is thermomechanically pulped fibre (preferably unbleached) comprising bundles of 3-5 cells so that the individual fibres have a length up to 5mm. Other examples of lignocellulose which may be used include chips, plant stem segments, whole plant stems. Sources of plant material for modification treatment include wood, straw, flax, linseed, bagasse, sisal, jute, kenaf, miscanthus and hemp.

The modified lignocellulose materials are eminently suitable for absorption of hydrophobic water-immiscible liquids. In particular, they are capable of absorbing up to 50 times their own weight of hydrophobic water-immiscible liquids from a spillage thereon in water and will retain 30 times their own weight when removed from water and allowed to drain. There is the additional advantage that the modified lignocellulose forms a discrete mass of hydrophobic water-immiscible liquid and modified lignocellulose which floats on clean water whereas untreated lignocellulose fibre forms a mass of hydrophobic water-immiscible liquid and unmodified lignocellulose which floats on an emulsified hydrophobic liquid/water mixture. In other words, use of untreated fibre causes oil to be "dragged" into the water whereas the modified lignocellulose leaves the water "clean". This has considerable implications for the clean-up of hydrophobic water-immiscible spillages in inland waterways or in areas where environmental protection is important. The chemically modified lignocellulose has the further advantage, over untreated fibres, in that it is less biodegradable and therefore less likely to deteriorate during storage.

The modified lignocellulose may be present d for use in the absorption of hydrophobic water-immiscible liquids in a number of



different forms. For example, the modified lignocellulose may be contained within an outer "covering" through which the liquid may pass. Such a "covering" could for example be a net or porous sheet. It is therefore possible to provide the modified lignocellulose in the form of a boom or pillow, i.e. a form in which oil absorbents are commonly used for cleaning oil spillages in water. To clean-up an oil-in-water spillage the boom or pillow is simply drawn through the water. Alternatively particulate modified lignocellulose may be spread onto water surface by dropping from an aircraft. Alternatively, particulate modified lignocellulose can be blown onto the water surface.

It is also possible to provide the modified lignocellulose in sheet form (eg a paper or fabric). Thus for example a sheet of lignocellulose material may be rendered attractive to hydrophobic water-immiscible liquids by any of the abovementioned treatments (eg acetylation) and used for cleaning up spillages of hydrophobic water-immiscible liquids, particularly spillages from machines or vehicles.

It should however be appreciated that the use of the modified lignocellulose is not restricted to the clean-up of spillages. The modified lignocellulose could for example be used in filters designed to separate and recover hydrophobic water-immiscible liquids from hydrophobic water-immiscible liquid and water mixtures.

---

**EXAMPLE OF PRODUCTION OF ACETYLATED LIGNOCELLULOSE (From EP-A-0 213 262 Example VII)**

Spruce thermomechanical fibre pulp (TMP) was dipped for 1 minute in liquid acetic anhydride. Excess anhydride was squeezed out from the pulp by applying mechanical compression forces to the material yielding an acetic anhydride to fibre pulp ratio of 2.5 w/w. The impregnated pulp was then heated at 120°C for different times. After the reaction a vacuum was applied. The fibre pulp was then air conditioned.

Sample	Reaction Time at 120°C (hours)	Weight gain due to acetylation (%)
Spruce TMP	0.5	11.7
	1.0	22.4
	2.0	24.8
	4.0	36.5

**LAB TESTS TO ILLUSTRATE THE USE OF ACETYLATED TMP IN CLEANING UP AN HYDROPHOBIC WATER-IMMISCIBLE LIQUID SPILLAGE**

**EXAMPLE 1: THE REMOVAL OF OIL FROM SEA-WATER**

In all of the following tests the hydrophobic water-immiscible liquid used was Medium Fuel Oil, the modified lignocellulose was thermo-mechanically pulped

wood fibre acetylated in accordance with the method described above and with an acetyl weight gain of between 14% and 17% and the sea-water was collected from the Irish Sea off Anglesey.

Medium fuel oil retention (weight gain expressed as multiple of initial fibre weight). Method adapted from European Patent No. 009436 p. 7. Briefly this adapted method was as follows: 5gms of fibre were mixed with 200ml of medium fuel oil and 200ml of sea-water. The mixture was stirred for 5 minutes using a rotary stirrer. The mixture was allowed to stand for 5 minutes and then poured through a screen. The liquid containing absorption agent collected on the screen and was allowed to drain for 5 minutes. The liquid containing fibre was weighed and the ratio of liquid to fibre weight calculated.

OIL/SEA WEIGHT GAIN BY FIBRES  
(multiple of initial fibre weight)

ACETYLATED FIBRE	28.9
UNTREATED FIBRE	25.8

The fibre-oil-water mixtures were vacuum dried over silica gel for 20 days. The acetylated fibre-oil-water mixture lost 4.5% of the oil-water weight. The untreated fibre lost 19.5% of the oil and water weight. A control beaker of oil in the desiccator lost 0.4% by weight over the same period. Graph 1 shows the rate of weight loss of the fibres and controls in the desiccator. The losses over silica gel from both untreated and acetylated fibres were therefore predominantly water. Thus, although the overall weight gain by both untreated and acetylated fibres was similar, the oil uptake of the acetylated fibres was greater.

Floatation trials in sea-water. Untreated fibre sank completely in sea-water after 2 days. Acetylated fibre started to sink in sea-water after 5 days. A slowly reducing proportion of the acetylated fibre continued to float for up to a month.

Acetylated fibre which previously absorbed oil floated on sea-water for at least two months.

Effect on water quality. The effect of the absorption of oil by the untreated and acetylated fibres on water quality below the main fibre mass has been assessed using two methods: extraction and weight measurement; and, extraction and UV absorption.

Method 1. Extraction and Weight Measurement. Fibres were mixed with oil and sea water in the ratio 5gm fibres:100ml oil:1000ml sea-water. A water sample from below the main fibre/oil mass was taken in a 100ml syringe. The oil was extracted from the sea-water by mixing with 100ml of chloroform. Sea-water was used as a control. The chloroform was separated from the water and samples of the chloroform evaporated. The weight of the remaining residue, expressed as a percentage of the chloroform sample, was:

untreated fibre	0.098%
acetylated fibre	0.006%
sea-water control	0.010%

Approximately 1.5% of the 100ml of oil stirred into the untreated fibre/oil/seawater mixture is emulsified by the untreated fibres.

6.

Method 2. Extraction and UV Absorption. UV peak absorbance of the chloroform extract is 100 times greater for the extract from the untreated fibre mixture than for the extract from the acetylated fibre mixture.

**EXAMPLE 2: THE REMOVAL OF WHITE SPIRIT FROM DEIONISED WATER**

In the following test the hydrophobic water-immiscible liquid used was White Spirit and the modified lignocellulose was thermo-mechanically pulped wood fibre acetylated in accordance with the method described above and with an acetyl weight gain of between 14% and 17%.

White spirit retention (weight gain expressed as multiple of initial fibre weight). Method adapted from European Patent No. 009436 p. 7. Briefly this adapted method was as follows: 5gms of fibre were mixed with 200ml of white spirit and 200ml of deionised water. The mixture was stirred for 5 minutes using a rotary stirrer. The mixture was allowed to stand for 5 minutes and then poured through a screen. The liquid containing absorption agent collected on the screen and was allowed to drain for 5 minutes. The liquid containing fibre was weighed and the ratio of liquid to fibre weight calculated.

**WHITE SPIRIT/WATER WEIGHT GAIN BY FIBRES**  
(multiple of initial fibre weight)

ACETYLATED FIBRE	15.7
UNTREATED FIBRE	17.9

The remaining white spirit and water which had not been absorbed by the fibre was collected, separated and the water and white spirit fractions weighed. From the weights of these fractions the uptake of the water by the fibre and the uptake of white spirit by the fibre were calculated. These values (expressed as a percentage of the total uptake) are shown below.

	WATER UPTAKE (%)	WHITE SPIRIT UPTAKE (%)
ACETYLATED FIBRE	19	81
UNTREATED FIBRE	63	37